

Biofuel production processField of invention

5 The present invention relates to a method for producing a biofuel, along with an apparatus for conducting such a method. In particular, the invention relates to a method and apparatus for producing sustainable aviation fuel (SAF).

Background

10 There is a growing need to produce sustainable routes to commonly used fuels such as aviation fuel. For example, the UK government has set a target that 10% of all aviation fuel should be sustainable aviation fuel by 2030. However, current methods for producing sustainable aviation fuel are on course to fall short of this target.

15 Sustainable fuels can be produced by a number of methods. For example, waste vegetable oils and fats (e.g. cooking oils) are known to be converted to aviation fuel. However, there is a limited volume of waste oils meaning there are insufficient quantities to rely on this as the sole solution, and the high monetary value means this is unlikely to be cost-effective. Biomass gasification also offers a route to fuel production, however, gasification can be a very energy intensive process and requires a dry feedstock, which limits its overall sustainability.

20 In WO 2018/076093 A1, a process based on hydrothermal liquefaction (HTL) treatment for co-processing high-water-content wastewater sludge and other lignocellulosic biomass is described for the co-production of biogas and bio-crude oil.

In US 2021/0214633 A1, hydrothermal liquefaction systems and methods of converting organic matter or biomass into biocrude oils and gases are described.

30 In CN 116554912 A, a method for producing substance oil through hydrothermal liquefaction of sludge, catalyzed by steel slag, is described.

In CN115180790A, the preparation of bio-oil from sludge is described according to a method comprising conditioning and continuous hydrothermal liquefaction.

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In EE 202100001 A, a method and system is described for the hydrothermal liquefaction and gasification of biomass using cavitation. This enables biomass to be converted into chemical raw materials suitable for the production of fuel and organic chemicals. In cavitation, rapid changes in liquid pressure cause the liquid to form small vapor-filled bubbles ("caverns") in places where the pressure is relatively low. Pressures of up to 15 bar are described.

Processing bio-oil to provide a hydrocarbon fuel is not disclosed in the documents described above.

In CN116179232A, a system of municipal sludge liquefaction coupled with upgrading and preparation of liquid fuel is described, characterized in that it includes a hydrothermal liquefaction reaction unit and a separation unit, a hydrogenation upgrading and re-separation unit, and a washing unit. Hydrothermal liquefaction of sludge at pressures lower than those described herein is used to obtain a mixed oil phase of bio-crude dichloromethane.

In the search for a more environmentally friendly and sustainable solution, there arises a need to transition to a waste to fuels scheme that uses widely available, low-cost feedstocks and a relatively low energy process.

It is an object of the present invention to obviate or mitigate one or more of the above-mentioned disadvantages. The present invention provides an alternative or more efficient waste to fuels scheme.

Summary of the invention

Hydrothermal processing of carbonaceous feedstocks such as used plastics or wood pulp presents one alternative route to generate sustainable fuels. Various conditions and feedstocks have been explored for hydrothermal processing, an example of such work being EP2718404B2. However, very limited work has been done on producing cost effective fuels using very low value feedstocks such as sewage sludge. Sewage sludge is a particularly challenging feedstock due to the high content of water, ash, and other components in the feedstock.

Accordingly, in the first aspect of the invention there is provided a method for producing a hydrocarbon fuel. The method may comprise subjecting the slurry of waste material to a hydrothermal liquefaction reaction to obtain a hydrothermal liquefaction product. The waste material may comprise one or more of sewage sludge, animal slurry, microalgal culture pastes, paper mill and palm oil mill effluents, and abattoir waste. The method may comprise separating a bio-oil from the hydrothermal liquefaction product. The method may comprise processing the upgraded bio-oil to provide a hydrocarbon fuel.

The term "slurry" is well known in the art but for the avoidance of doubt is used herein to indicate a mixture where solid particles are dispersed within a liquid (e.g. the solid particles may be from sewage sludge). For example, the slurry may be an aqueous slurry. Aqueous slurries are advantageous, since they provide a greener and cost-effective solution which avoid the use of potential harmful industrial solvents and chemicals.

Specifically, it has been found possible to produce a bio-oil, i.e. a synthetic liquid hydrocarbon derived from biomass, starting from waste material, and then subsequently upgrade this to produce a high value hydrocarbon fuel. Advantageously, the method described herein allows for a reasonable yield of high-value hydrocarbon fuel (such as sustainable aviation fuel) to be produced from an extremely low value feedstock. The method may also not require expensive and energy intensive pre-treatment steps, such as drying out the feedstock, which often negates the environmental gains in prior art methods such as gasification. Further, in some embodiments, the method may be capable of producing the initial bio-oil without the need for adding a catalyst or the addition of organic solvents, to the hydrothermal liquefaction reaction. Advantageously, this provides a greener and more cost-effective solution than prior art methods, and avoids needing to separate a catalyst from the reaction products.

The hydrocarbon fuel may be one or more of: sustainable aviation fuel, marine fuel, road fuel, heating fuel, or generator fuel. Preferably, the hydrocarbon fuel comprises sustainable aviation fuel. In some embodiments the method may be adjustable such that the hydrocarbon fuel output may be selectable by an operator. E.g. the hydrothermal liquefaction operating parameters may be selected in order to promote the formation of a specific hydrocarbon fuel.

The inventors have found that carrying the hydrothermal liquefaction reaction out under particular conditions, in particular with a residence time of 15 to 25 minutes, at a temperature of 280 to 373°C and a pressure of from 18 MPa to 22 MPa, unexpectedly leads to the production of a greater ratio of bio-oil to bio-char, with the bio-oil having properties that are particularly advantageous for applications as a sustainable aviation fuel (SAF).

The method may comprise preparing a slurry of waste material e.g. prior to hydrothermal liquefaction. Preparing a slurry may comprise adding a diluent to the waste material. The diluent may comprise water. The method may comprise mixing or homogenising the slurry.

In one series of embodiments, the waste material comprises sewage sludge. The sewage sludge may comprise treated sewage sludge, for example sewage sludge treated by anaerobic digestion, such as conventional anaerobic digestion or advanced anaerobic digestion, and/or thermal hydrolysis. In some embodiments, the sewage sludge comprises post-anaerobic digested sewage sludge (also known as digested cake). Additionally, or alternatively, the sewage sludge may be taken from alternative points within the wastewater treatment system. The method of the present invention therefore utilises a feedstock which would otherwise be considered landfill waste while also generating a highly desirable product.

Furthermore, the process can produce other useful products such as bio-char. Bio-char is a useful soil amendment which can improve agricultural yields as well as sequestering carbon, either through soils or by directly burying the bio-char. Overall, the method of the invention provides a highly effective and “green” method for hydrocarbon fuel production, and especially for aviation fuel production.

The term “digested cake” is well known in the art but for the avoidance of doubt is used herein to indicate an end material of the domestic sewage, industrial, and commercial wastewater treatment process obtained after anaerobic digestion. Digested cake may also be known as treated sludge, biosolids or digested sludge. Digested cake is distinct from primary sludge or activated sludge, which are produced earlier in the water treatment process. Typically, digested cake has a solids (e.g. dry solids) content of from 15 wt% to 40 wt%, e.g. 20 wt% to 30 wt%. Preferably, the digested cake has a solids

(e.g. dry solids) content of from 23 wt% to 28 wt%, for example 26 wt%. In some embodiments the sewage sludge is produced exclusively from digested cake and a diluent, e.g. water. In other words, the sewage sludge consists of digested cake, or is digested cake.

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The direct utilisation of the digested cake feedstock, with a relatively high water content, allows for a hydrocarbon fuel (e.g. sustainable aviation fuel) to be produced without the energy intensive pre-treatment step of drying out the feedstock, which is typically required in other recycling processes.

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The term "hydrothermal liquefaction" is also well known in the art but for the avoidance of doubt is used herein to indicate a process wherein the carbonaceous feedstock is hydrolysed or degraded by means of water at a certain temperature and pressure. This process typically involves subjecting the feedstock to a temperature in the range of from 200°C and 400°C and a pressure of from 10 MPa to 40 MPa (100 to 400 bars) for a specified period of time.

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In a series of embodiments, the slurry of waste material has a dry solids content of 20 wt% or less. The slurry of waste material may have a dry solids content of from 1 - 20 wt%, 2-20 wt%, 5-20 wt%, 10-20 wt%, 12-18 wt%, 14-16 wt%, or approximately 15 wt%. It will be understood that end points of ranges throughout this description may be combined in any manner.

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Utilising a low concentration slurry has been shown to result in a surprising and counter intuitively high yield of bio-oil. This is an improvement over the state of the art in which low concentration feedstocks typically result in lesser yields and a less economical process. As a result, prior art methods such as EP2718404B2 choose to incorporate organic solvents to help achieve homogenization and allow them to operate at higher concentrations. For example, the inventors of EP2718404B2 use a 25% slurry of Dry Distillers Grain in their examples. Without wishing to be bound by theory, the high yield of bio-oil is thought to arise due to the stability of the slurry. The inventors have surprisingly found that using a reduced solids content does not restrict the hydrolysis of the biomass and shifts the relative proportions of the hydrothermal liquefaction to provide a higher yield of bio-oil and to the detriment of bio-char production.

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In some embodiments, the hydrothermal liquefaction reaction comprises subjecting the slurry of waste material to a temperature of from 280 to 373°C. The temperature may be 290 to 370°C, 295 to 360°C, 300 to 350 °C, 310 to 340°C, 320 to 330°C or 325°C.

5 In some embodiments, the hydrothermal liquefaction reaction comprises subjecting the slurry of waste material to a pressure of from 18 MPa to 22 MPa (180 to 220 bar). The pressure may be 19 to 21MPa, or 20MPa. In some embodiments, the temperature may be lower than the critical temperature of water.

10 The slurry of waste material may have a residence time of 5 to 60 minutes in the hydrothermal liquefaction conditions. The residence time may be at least 10, 12, 14, 15, 16, 18, or 20 minutes. The residence time may be less than 50, 40, 30, or 25 minutes.

In some embodiments, the residence time is less than 25 minutes and/or at least 10, 12, 15, 16, 18 or 20 minutes. In particular embodiments, the residence time is 15 to 25 minutes. The inventors have found that this residence time unexpectedly provides a greater ratio of bio-oil to bio-char, with the bio-oil having properties that are particularly advantageous for applications as a sustainable aviation fuel (SAF).

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20 In one series of examples, the hydrothermal liquefaction temperature may be 325°C, the pressure 20MPa and the residence time 20 minutes. The above temperature, pressure and residence time ranges have been found to unexpectedly maximise the yield of bio-oil.

25 In some embodiments, the method is a batch process. In alternative embodiments, the method is a continuous process.

The separation may comprise using an organic solvent e.g. to separate the bio-oil from the hydrothermal liquefaction product. In some embodiments, the organic solvent is one or more of hexane, cyclohexane, acetone, dichloromethane, and ethyl acetate. In some
30 embodiments, the organic solvent is one or more of hexane, cyclohexane, acetone, or dichloromethane. The organic solvent may be separated (e.g. from the bio-oil) via evaporation. The organic solvent may be reclaimed and recycled. Solvent separation may provide a high yield method for separating the bio-oil and/or may consume less
35 energy than other separation methods.

- Alternatively, separating the bio-oil from the hydrothermal liquefaction product may be carried out without the use of solvents, for example by filtration or centrifugal separation (wherein the centrifugal force is used to accelerate the settling rate of particles and to separate particles according to size, shape and specific gravity), e.g. with a centrifuge, such as an oil centrifuge, or with a cyclone, such as a hydrocyclone. In some embodiments, a centrifuge is used to separate the bio-oil from the hydrothermal liquefaction product.
- 10 The method may further comprise separating a bio-char from said hydrothermal liquefaction product. Biochar in itself may be a desirable product of the process. The method may comprise processing the bio-char to obtain a refined bio-char. The refinement may comprise extracting further bio-oil from the biochar. In particular embodiments, the bio-char is separated from the hydrothermal liquefaction product at elevated pressures. The inventors have found that separation of the bio-char from the other hydrothermal liquefaction products is particularly effective at enhancing bio-oil yield when conducted at elevated pressure.
- 20 In particular embodiments, a hydrocyclone is used to remove biochar from the hydrothermal liquefaction product and then a centrifuge is used to separate the bio-oil from the residual aqueous component. These embodiments are particularly advantageous when separating the bio-oil from the hydrothermal liquefaction product at large scale, e.g. when separating the bio-oil from at least one tonne per day of hydrothermal liquefaction product.
- 25 In some embodiments, processing the bio-oil to provide a hydrocarbon fuel comprises hydrotreating the bio-oil. Hydrotreating the bio-oil may comprise hydrodeoxygenation, hydrodesulfurization and hydrodenitrogenation of the bio-oil. In some embodiments, hydrotreating the bio-oil comprises hydrodeoxygenation of the bio-oil. In some embodiments, hydrotreating the bio-oil comprises hydrodeoxygenation, hydrodesulfurization and hydrodenitrogenation of the bio-oil. The reaction, such as the hydrodeoxygenation reaction, may be carried out at a temperature of from 360 to 400°C. The temperature may be 365-395°C, 370-390°C, 375-385°C, or 380°C. The reaction, such as the hydrodeoxygenation reaction, may be carried out at a pressure of from 10MPa to 13MPa (100-130 bar) e.g. 10-12MPa, 10.5-11.5MPa, or 11MPa. The reaction,
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such as the hydrodeoxygenation reaction, may be carried out in the presence of a catalyst e.g. a transition metal-based sulphided catalyst such as NiMo and NiW based catalysts. The hydrotreatment may be configured to maximise the yield of a desired hydrocarbon fuel, such as sustainable aviation fuel.

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Processing the bio-oil to provide a hydrocarbon fuel may comprise fractionation of and/or hydrocracking the bio-oil. Fractionation and/or hydrocracking of the bio-oil may be configured to maximise the yield of a desired hydrocarbon fuel, such as sustainable aviation fuel. In some embodiments, the fractionation and/or hydrocracking may produce
10 a first hydrocarbon fuel and a heavy fuel. The first hydrocarbon fuel may comprise an aviation fuel. The method may further comprise recycling the heavy fuel to the fractionation and/or hydrocracking reactions to increase the yield of the first hydrocarbon fuel. Recycling of the heavy fractions increases the yield of a desired product and reduces the energy cost per unit of desired product. In some embodiments, the
15 fractionation and/or hydrocracking of the bio-oil may also produce a bio-naphtha. Bio-naphtha is a further desirable product and can be further processed and/or separated, or used as a chemical feedstock or as a fuel.

In some embodiments, the hydrothermal liquefaction reaction and/or the separation of
20 the hydrothermal liquefaction reaction product produces off-gases. The method may comprise oxidising or combusting (e.g. burning) the off-gases or a component thereof in a heat recovery unit. For example, the off-gases may be used for heat and/or energy generation. The method may further comprise supplying heat and/or energy to the hydrothermal liquefaction reaction from the combustion of the off-gases in the heat
25 recovery unit. This improves the overall efficiency of the process while minimising potentially harmful emissions. Additionally or alternatively, the off-gases or a component thereof may be used as a feedstock (e.g. a C1 feedstock) for the production of syngas and/or fine chemicals. The off-gas is typically rich in CO₂ and short chain hydrocarbons (e.g. C1-C6) and can be separated or can undergo further processing and use.

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According to a second aspect of the invention, there is provided a hydrocarbon fuel produced according to the method described herein. The hydrocarbon fuel may be a sustainable aviation fuel.

The inventors have found that aviation fuel produced according to the above process may contain relatively high levels of aromatics, cyclo-, linear, and branched (e.g. iso-) paraffinic hydrocarbons. Such compositions may be advantageous over alternative synthesis routes for generating sustainable aviation fuel e.g. allowing a lower proportion of fossil jet fuel be used in sustainable aviation fuel blends. The hydrocarbon fuel may have a content of n-alkanes of greater than 10 wt% e.g. more than 12, 14, 15, 16, 18 or 19 wt%. In some embodiments, the hydrocarbon fuel has a content of n-alkanes of greater than 16 wt% e.g. more than 17, 18 or 19 wt%. The hydrocarbon fuel may have a content of n-alkanes of less than 30 wt% e.g. less than 28, 26, 25, 24, 22, or 20 wt%.

The hydrocarbon fuel may have a content of iso-alkanes of greater than 5 wt% e.g. more than 6, 7, 8, 9, 10, 12, 14, or 15 wt%. In some embodiments, the hydrocarbon fuel has a content of iso-alkanes of greater than 8 wt%, e.g. more than 9, 10, 11, 12, 13, 14 or 15 wt%. The hydrocarbon fuel may have a content of iso-alkanes of less than 25 wt% e.g. less than 24, 22, 20, 18, 16, 15, 14, 12 or 10 wt%. In some embodiments, the hydrocarbon fuel has a content of iso-alkanes of less than 20 wt%, e.g. less than 19, 18, 17, 16 or 15 wt%. The hydrocarbon fuel may have a content of monocycloalkanes greater than 10 wt% e.g. more than 12, 14, 15, 16, 18, or 20 wt%. In some embodiments, the hydrocarbon fuel has a content of monocycloalkanes greater than 15 wt% e.g. more than 16, 17, 18, 19 or 20 wt%. The hydrocarbon fuel may have a content of monocycloalkanes of less than 40 wt% e.g. less than 38, 36, 35, 34, 32, or 30 wt%. In some embodiments, the hydrocarbon fuel has a content of monocycloalkanes of less than 38 wt% e.g. less than 37, 36, 35, 34, 32, 30, 29, 28, 27, 26, 25, 24, 23, 22 or 20 wt%. The hydrocarbon fuel may have a content of polycycloalkanes greater than 5 wt% e.g. greater than 6, 7, 8, 9, or 10 wt%. In some embodiments, the hydrocarbon fuel has a content of polycycloalkanes greater than 7 wt% e.g. greater than 8, 9, 10, 11, 12, 13, 14, 15 wt%. The hydrocarbon fuel may have a content of polycycloalkanes less than 35 wt% e.g. less than 34, 32, 30, 28, 26, or 25 wt%. The hydrocarbon fuel may have a content of aromatic compounds greater than 10 wt% e.g. greater than 12, 14, 15, 16, 18 or 20 wt%. The hydrocarbon fuel may have a content of aromatic compounds less than 30 wt% e.g. less than 28, 26, 25, 24, 22, or 20 wt%. In some embodiments, the hydrocarbon fuel has a content of aromatic compounds less than 25 wt% e.g. less than 20 or 10 wt%. The inventors have found that certain conditions provide hydrocarbon fuel with a relatively low aromatic content, e.g. less than 20 wt%. This has the advantage of reducing sooting of the fuel when combusted, e.g. in a jet engine.

According to a third aspect of the invention, there is provided an apparatus for producing sustainable aviation fuel. The apparatus may comprise a hydrothermal liquefaction reactor. The reactor may be configured to receive the slurry of waste material and conduct a hydrothermal liquefaction reaction on the slurry to produce a hydrothermal liquefaction product. The apparatus may comprise a separation unit e.g. configured to receive the hydrothermal liquefaction product and separate a bio-oil from the hydrothermal liquefaction product. The apparatus may comprise a processing unit configured to receive the bio-oil and process the bio-oil to produce a hydrocarbon fuel. The hydrocarbon fuel may be a sustainable aviation fuel.

The apparatus may comprise a mixer configured to prepare a slurry of waste material. The mixer may comprise a diluent inlet for mixing a diluent with the waste material. The diluent may comprise water. The mixer may be configured to homogenise the slurry.

Additionally or alternatively, the hydrocarbon fuel may be a sustainable gasoline fuel.

The processing unit may comprise a hydrotreating unit configured to hydrotreat the bio-oil.

The processing unit may comprises a fractionation unit configured to separate the bio-oil to provide a sustainable aviation fuel and other fuel products. Additionally or alternatively, the processing unit may comprise a hydrocracking unit configured to crack the bio-oil. For example, the hydrocracking unit may be configured to provide a sustainable aviation fuel and other fuel products.

The processing unit may comprise a recycling line configured to recycle at least some of the other fuel products to the fractionation unit, hydrocracking unit, and/or hydrotreating unit.

The processing unit may comprise a heat recovery unit configured to burn off gases produced from the hydrothermal liquefaction reaction. The heat recovery unit may be configured to supply energy to the hydrothermal liquefaction reactor and/or the processing unit.

For avoidance of doubt, it will also be appreciated, where appropriate, that any embodiments as described herein in relation to one aspect of the present invention will also apply to the other aspects of the present invention.

5 Brief description of figures

The invention will now be described with reference to the following figures, in which:

Figure 1 is a process flow diagram showing an embodiment of the present invention;

Figure 2 is a graph showing the temperature and pressure profile of a hydrothermal liquefaction (HTL) experiment;

10 Figure 3 is a graph showing the effect of reaction temperature on the bio-oil and bio-char yields;

Figure 4 is a graph showing the effect of residence time on the bio-oil and bio-char yield;

15 Figure 5 is a graph showing the effect the dry solids content of the slurry on the bio-oil and biochar yield;

Figure 6 is a graph showing the difference in bio-oil and bio-char yield obtained at 20 MPa (200 bar) compared to 18 MPa (180 bar).

Figure 7 is a graph showing the effect of the feedstock on the bio-oil and biochar yield; and

20 Figure 8 is a simulated distillation curve for a hydrotreated bio-oil sample.

Detailed description

The aspects of the present invention will now be further described by various non-limiting examples and with reference to the enclosed figures.

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Method and System Overview

Figure 1 shows a process flow diagram of a method for producing biofuels. A sample of feedstock (in this case, digested cake 101) is mixed with water 102 in mixer 110 to prepare slurry 111. The slurry is loaded into a hydrothermal liquefaction reactor 120 and hydrolysed at elevated temperatures and pressures (e.g. a temperature of 325°C and a pressure of 20 MPa (200 bar)) to produce a hydrothermal liquefaction product 121 and off gases 122. The hydrothermal liquefaction products 121 are fed to separation unit 130 and separated into a bio-oil 131, a bio-char 132, a waste water stream 133 and any further off gases 134. The off gases 122, 134 are fed to a heat recovery unit 200 where

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they are combusted and the heat energy obtained used to provide some of the energy for the hydrothermal liquefaction reaction.

5 The bio-oil 131 is pre-treated 140 with hydrogen 181, obtained from hydrogen storage 180, and then hydrotreated 150 (e.g. exposed to a reaction, such as a hydrodeoxygenation reaction, at a temperature of from 360 to 400 °C and a pressure of from 10 to 13 MPa with a transition metal-based sulphided catalyst e.g. a NiMo or NiW based catalyst) to provide an upgraded bio-oil 151 with a reduced oxygen content compared to bio-oil 131. The upgraded bio-oil 151 may further comprise a reduced
10 nitrogen and/or sulfur content compared to bio-oil 131. A further waste water stream 152 is also obtained. The upgraded bio-oil 151 is then fed to a fractionation and stabilisation unit 160 where the upgraded oil 151 is separated based on boiling point into a sustainable aviation fuel fraction 161, a bio-naphtha fraction 162, a heavy fuel fraction 163 and a remaining fraction 164. The sustainable aviation fuel, bio-naphtha and heavy
15 fuel fractions are sent for storage and subsequent use. The remaining fraction may enter a hydrocracking unit 170 configured to break down the very heavy hydrocarbons in the presence of hydrogen 183 to increase the yield of lighter fuel products. The hydrocracked products 171 are separated and mixed with the sustainable aviation fuel 161, a bio-naphtha 162, and heavy fuel 163 streams. Any unusable products 174 may be recycled
20 to the hydrotreating unit 150 for further processing.

The bio-char 132 which was separated from the hydrothermal liquefaction products 121 may be further treated 190 to provide a refined bio-char 191. Any bio-oil 192 obtained from the refinement of the bio-char is mixed with bio-oil 131 in pre-treatment step 140.
25 Waste water 193 from the refinement of the bio-char, along with the other waste water streams 133, 152, 165 are combined and sent for waste water treatment 210.

Feedstock

30 Sewage sludge was collected from a sewage treatment facility in Avonmouth in the summer of 2021. Samples of sewage sludge were collected from different points of the wastewater treatment process according to **Table 1** below:

Feedstock Name	Solids content
Digested Cake Sample 1	26.0 wt. %
Digested Cake Sample 2	22.8 wt. %

Activated Sludge	4.9 wt. %
Thickened undigested sludge	4.6 wt. %

Table 1 – Example sewage sludge feedstocks

Sewage Sludge Characteristics	Value
Particle size & distribution	1.5-1,100 µm
Particle shape (round / flat)	irregular
Total Solids	25wt%
Density of mixture @ Room Temp	1.113 kg/m ³
Specific Heat Capacity of mixture	0.0153 kJ/kg-K
Vapour pressure for volatile components	1X10 ⁰⁴ to 0.67 bara

Table 2a – Characterisation of average Digested Cake samples

- 5 Activated and thickened undigested sludge are both obtained after the primary sedimentation tanks and before the anaerobic digestion treatment. Thickened digested sludge has a thickener added thereto. Digested Cake Sample 1 was analysed for ash content and characterised using elemental analysis (CHNSO) and ICP-OES. The oxygen content was calculated by difference ($100\% - \sum(\text{CHNS} + \text{ash})$). The results of the
- 10 characterisation are shown in **Table 2b**.

Component	wt. %	Inorganic elements	mg/kg
C	33.4	Al	7600
H	4.65	Ca	40000
N	3.78	Cr	30
S	0.80	Cu	250
O	18.87	Fe	17000
Ash	38.5	K	1200
		Mg	5800
		Mn	220
		Na	670
		Ni	16
		P	18000
		Si	52
		Sn	29
		Ti	4.0
		Zn	710
		Zr	0.53

Table 2b – Characterisation of Digested Cake Sample 1

The reproducibility of the sewage source was investigated by analysing digested cake samples from a sewage treatment facility collected over the course of 54 consecutive

weeks from June 2022-June 2023 and comparing the composition of the samples. The results are shown in **Table 2c**.

Component	Units	Mean	SD
C	wt. %	34.99	1.40
H	wt. %	5.30	0.23
N	wt. %	4.85	0.34
S	wt. %	1.27	0.23
O	wt. %	21.61	1.20
Ash	wt. %	31.98	2.48
Al	mg/kg	6525.83	1531.91
Ca	mg/kg	49762.96	11492.96
Cr	mg/kg	40.28	7.97
Cu	mg/kg	351.11	71.94
Fe	mg/kg	22760.20	3152.41
K	mg/kg	1357.89	354.85
Mg	mg/kg	5841.73	1742.36
Mn	mg/kg	269.44	46.71
Na	mg/kg	937.65	451.04
Ni	mg/kg	22.72	4.54
P	mg/kg	26161.11	6242.62
Si	mg/kg	640.52	254.92
Sn	mg/kg	29.06	6.28
Ti	mg/kg	5.72	4.51
Zn	mg/kg	938.81	178.44
Zr	mg/kg	1.12	0.55
As	mg/kg	9.24	1.92
Cd	mg/kg	3.65	1.98
Co	mg/kg	5.24	1.27
Pb	mg/kg	82.11	37.22
Hg	mg/kg	0.59	0.44
Mo	mg/kg	7.81	2.27
Se	mg/kg	4.56	1.34
TI	mg/kg	0.44	0.23

Table 2c – Characterisation of digested cake samples taken from a sewage treatment facility over the course of 54 consecutive weeks from June 2022-June 2023.

Post-anaerobic digested sewage sludge (i.e. digested cake, also known as biosolids) is well-known to be an end product of the wastewater treatment process. It has a high water content and its uses are fairly limited. Currently, digested cake is primarily used as a fertiliser but recent regulatory changes will limit the use of such sewage sludge in agriculture applications; in some countries, disposal by this route has already been banned.

Preparation of slurries

Prior to hydrothermal liquefaction reactions, digested cake samples 1 and 2 were diluted with water to prepare slurries with specified solids content, as described in **Table 3**. In contrast, the comparative feedstocks of activated sludge and thickened undigested sludge were used as received due to their already low solids content.

Sample No	Feedstock	Preparation
E1	Digested Cake Sample 1	Diluted to produce slurry with a solid dry contents of 4.5 wt. %
E2	Digested Cake Sample 1	Diluted to produce slurry with a solid dry contents of 10 wt. %
E3	Digested Cake Sample 1	Diluted to produce slurry with a solid dry contents of 15 wt. %
E4	Digested Cake Sample 1	Diluted to produce slurry with a solid dry contents of 20 wt. %
E5	Digested Cake Sample 2	Diluted to produce slurry with a solid dry contents of 12.9 wt. %
C1	Activated Sludge	Used as received (solid dry contents of 4.9 wt. %)
C2	Thickened undigested sludge	Used as received (solid dry contents of 4.6 wt. %)

Table 3 – Samples used in example hydrothermal liquefaction reactions

Hydrothermal Liquefaction

Hydrothermal liquefaction reactions were conducted using a bench top high-pressure stirred reactor system, such as a Parr series 4560 with 300 mL of volume. A pressure regulator was installed to allow control of the reactor pressure and isobaric operation. The maximum operation conditions of the batch reactor was 200 bar at 350°C. Typically, the maximum operation conditions of the batch reactor would be 180-220 bar at 300-350°C. These conditions fall into a subcritical range for water and are easier and less expensive to achieve than supercritical conditions (>373°C, 220bar).

In a typical experiment, about 200 g of sewage sludge slurry was loaded into the reactor. The reactor was purged three times with nitrogen and pressurized with nitrogen at 100

bar at room temperature. The temperature was then increased to reach the target temperature using the Parr reactor controller programmable settings. After the residence time was achieved the reactor was left to cool down to 200 °C and then quenched with cold water to room temperature. The reactor was then depressurized.

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Figure 2 presents the temperature heating and pressure profile of a HTL experiment performed on sample E3 at reaction temperature of 325 °C at 180 bar with a residence time of 20 minutes. The red points show the pressure over time and the black points show the temperature over time.

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Separation of hydrothermal liquefaction products

To separate the products of the hydrothermal liquefaction reactions, dichloromethane was added to the mixture of products and the resultant liquid phase was separated from the solid phase by filtration. The solid (corresponding to the bio-char) was dried overnight at 85 °C and the weight was measured. The liquid was allowed to separate into an aqueous phase and an oil phase and the two phases were then separated by decantation. A rotary evaporator was used to remove the dichloromethane from the oil phase to yield a bio-oil. The bio-oil was left to dry overnight at 85 °C and the weight of bio-oil was measured. Alternatively, separation of phases may be carried out by centrifugation e.g. such as using a horizontal solid bowl centrifuge performing a three-phase separation.

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Calculation of bio-oil yield from hydrothermal liquefaction reaction

HTL bio-oil yield was defined as the ratio of the weight of bio-oil produced to the weight of sewage sludge, dry solid basis, using equation 1:

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$$Bio\ oil\ yield = \frac{weight\ of\ Bio-oil}{weight\ of\ sewage\ sludge} \times 100 \quad (1)$$

Bio-char yield was defined as the ratio of the weight of bio-char produced to the weight of sewage sludge, dry solid basis, using equation 2:

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$$Liquefaction\ Biochar\ yield = \frac{weight\ of\ char}{weight\ of\ sewage\ sludge} \times 100 \quad (2)$$

Hydrotreatment of the bio-oil

Hydrotreatment was carried out on the bio-oil received from the separation unit 130 and as described in subsequent sections (see **Table 5** detailing the characterisation of the initial bio-oil). Hydrotreating involved a hydrodeoxygenation (dominant process) plus

35

concomitant hydrodesulphurization and hydrodenitrification reactions. The hydrodeoxygenation used a transition metal-based sulfided catalyst (e.g. a quadrilobe-shaped extrudates Ni/Mo catalyst supported on alumina (NiMoOx/ γ -Al₂O₃)) at a temperature between 360 and 450°C and a pressure between 10-20MPa. The hydrogen consumption was between 40-60 g per kg of bio-oil.

Fractionation and hydrocracking

Hydrocracking provides the cracking of long chain paraffinic compounds into shorter ones in the presence of transition metal-based catalyst (e.g. cylindrical-shaped extrudates dewaxing catalyst, Ni/W supported on acidic silica-alumina) at temperatures typically between 360 and 450°C, at pressures between 10-20MPa, in the presence of hydrogen. Conditions for hydrotreatment and hydrocracking may be adjusted by operators to optimise fuel yields, composition and properties.

Fractionation involves the separation of mixtures of paraffinic compounds i.e. linear, iso-, cyclic and aromatics in several fuel cuts based on boiling point ranges e.g. bionaptha cut (boiling point <150°C), jet fuel cut (boiling point between 140°C and 270°C), and a diesel cut (boiling point >270°C).

The upgraded bio-oil after hydrotreatment and hydrocracking was analysed using GC-MS/FID. The summarised results are shown in **Table 4** below.

Carbon range	Wt. %
C13	6.31
C14	6.58
C15	14.50
C16	17.96
C17	18.40
C18	20.23
C19	2.58
Others	13.41
Total	100
Aromatics	3.16
Oxygenated	6.31

Table 4 – GC-MS/FID summary of the upgraded bio-oil

The upgraded bio-oil in **Table 4** has a much lower proportion of longer-chain hydrocarbons and a lower proportion of oxygenated compounds.

Refinement of the bio-char

The biochar recovered after the separation of the liquid phase composed by the bio-oil and the HTL wastewater, may be washed with an organic solvent, e.g. hexane, cyclohexane, acetone, dichloromethane etc., to extract any remaining bio-oil. The organic solvent, is evaporated, the bio-oil is recovered, and the organic solvent reused in the process.

Effect of hydrothermal liquefaction reaction temperature

The effect of the hydrothermal liquefaction reaction temperature on the conversion of sewage sludge to bio-oil was investigated. Experiments were conducted on sample E3 using reaction temperatures of 300, 325 and 345 °C. The residence time and target pressure were fixed at 20 minutes and 18 MPa (180 bar) respectively.

Figure 3 shows the effect of reaction temperature on the yield of bio-oil and bio-char obtained from the hydrothermal liquefaction reaction. The data shows that the maximum bio-oil yield was achieved at 325 °C with a bio-oil yield of 29.1 wt.% and a bio-char yield of 41.2 wt.%.

Effect of hydrothermal liquefaction residence time

The effect of the residence time within the Hydrothermal Liquefaction reaction on the conversion of sewage sludge to bio-oil was investigated. Experiments were conducted on sample E3 with residence times of 10, 20 and 30 minutes. The reaction temperature was fixed at 325 °C and the target pressure was fixed at 18 MPa (180 bar).

Figure 4 shows the effect of residence time on the yield of bio-oil and bio-char. The results shows that the maximum bio-oil yield of was achieved at residence time of 20 minutes. The inventors found that an optimum residence time could be identified for maximum bio-oil production relative to biochar - surprisingly, both shorter and longer residences times enhanced the production of bio-char in detriment of bio-oil production. Without wishing to be bound by theory, it is believed that residence times shorter than 20 minutes did not achieve maximum conversion of the sewage sludge to bio-oil, while residence times longer than 20 minutes resulted in the bio-oil being further degraded to char, possibly due to secondary or tertiary reactions.

Effect of the dry solid content of the slurry on the hydrothermal liquefaction reaction

The effect of the dry solid content of the slurry on the conversion sewage sludge to bio-oil was investigated. Hydrothermal liquefaction reactions were conducted on samples E1-E4 (i.e. samples with a solid dry content (in wt.%) of 4.5, 10, 15 and 20). The hydrothermal liquefaction reaction parameters were fixed at a residence time of 20 minutes, a reaction temperature of 325 °C, and a target pressure of 180 bar. The HTL experiments were also conducted using the same stirring rate. The viscosity/thickness of the slurry increased with the increase of the dry solid content.

Figure 5 presents the effect of the solid dry content on the yields of bio-oil and bio-char. The maximum bio-oil yield was achieved with a dry solid content of 15 wt.%. Surprisingly, both lower and higher dry solid contents were seen to result in lower bio-oil yields. Without wishing to be bound by theory, it is believed that using slurries with dry solid contents higher than 15 wt.% might restrict the hydrolysis of the biomass, enhancing the production of bio-char in detriment of bio-oil production. Similarly, the lower yields from the slurries with a dry solids contents lower than 15 wt.% is suggestive of the hydrolysis also not being fully achieved. It therefore appears that the dry solid content in the slurry (i.e. water-to-biomass ratio) needs to be carefully optimised and is one of the most important parameters in the HTL reaction.

Using a low water content (i.e. a high dry solids content) would usually be considered as a method for enhancing the yield from the reaction, but to the detriment to the mechanical handling properties. However, it has been surprisingly found that a high solids content may promote the hydrolysis of biomass, leading to a lower yield of bio-oil and a higher yield of bio-char. The method may therefore be able to achieve high bio-oil yields without suffering from mechanical handling challenges.

Effect of hydrothermal liquefaction reaction pressure

The effect of the hydrothermal liquefaction reaction pressure on the conversion of sewage sludge to bio-oil was investigated. Experiments were conducted on sample E5 using target pressures of 18 MPa (180 bar) and 20 MPa (200 bar). The residence time and temperature were fixed at 20 minutes and 325 °C respectively.

Figure 6 shows the change in yield of bio-oil and bio-char yields obtained at 20 MPa (200 bar) in comparison with the values obtained at 18 MPa (180 bar). For comparison the bio-oil yield at 18 MPa (180 bar) was 18.7 wt.% and bio-char yield was 44.5 wt.%. The results suggest that increasing the pressure has a positive effect on the bio-oil production and a detrimental effect on the production of bio-char.

Choice of Feedstock

Samples of sewage sludge collected from different points of the wastewater treatment process were investigated for use in the hydrothermal liquefaction reaction. The samples tested were E3, E5, C1 and C2. C1 and C2 are comparative examples based on using activated sludge and thickened undigested sludge. Samples E3 and E5 comprises slurries of digested cake (i.e. post-anaerobic digested sewage sludge) formed by dilution of digested cake with deionised water. The hydrothermal liquefaction reaction parameters were fixed at a residence time of 20 minutes, a reaction temperature of 325 °C and a target pressure of 180 bar.

Figure 7 shows the yields of bio-oil and bio-char obtained from HTL reactions on the various sewage sludges analysed. The data shows that using E3, obtained from digested cake 1, has a higher bio-oil yield and a lower bio-char yield than the HTL reaction using E5. Without wishing to be bound by theory, this is believed to be due to natural variation in composition of the digested cake samples.

HTL reactions using comparative samples C1 and C2 (activated and thickened undigested sludge respectively) showed lower yields than when using E3. A key factor in this result is likely to be the lower dry solid contents of C1 and C2. However, while drying the activated and thickened undigested sludge samples to provide a more concentrated feedstock may potentially result in a higher bio-oil yield, drying the feedstocks to increase the solid dry content of the sludge would be high in energy consumption and be expensive. The drying process would significantly reduce the cost efficiency of the present invention due to the energy intensive pre-treatments. The results therefore show that digested cake is a highly desirable overall feedstock, providing the highest yields after only a simple dilution process, while minimising expensive pre-treatment processes.

Hydrothermal Liquefaction Product Characterisation

The bio-oil and bio-char obtained after separation of a hydrothermal reaction using sample E3 with a residence time of 20 minutes, a reaction temperature of 325 °C and a target pressure of 180 bar, were further analysed as detailed below.

5 Bio-oil

We found that the bio-oil generated typically contains a range of chemical species (**Table 4** below). The complexity of the bio-oil is expected to contribute to the range of hydrocarbon species in the resulting aviation fuel fraction, which may include higher levels of aromatics or iso- and cycloalkane hydrocarbons compared with sustainable
10 aviation fuels from some other routes.

Table 5 presents the weight percentage of the ranges of hydrocarbons and type of compounds, e.g. hydrocarbons, fatty acid methyl esters (FAMES), aromatics and others, based on the area percentages of the chromatogram peaks. The results for the bio-oil
15 composition show that the bio-oil is mainly composed by oxygenated and nitrogenous compounds. There is a considerable percentage are FAMES (19.1 wt.%) and plant cholesterol (34.6 wt.%).

Carbon range	Wt.%
<C10	12.9
C10-15	7.8
C16	5.0
C17	11.5
C18	2.1
C19-22	21.0
+C22	39.7

Table 5. Estimation of the weight percentages of the different types of hydrocarbons present in a
20 bio-oil obtained from a HTL reaction on sample E3, at 325 °C, 20 minutes of residence time and 18 MPa (180 bar) of pressure.

The bio-oil sample was also analysed for ash content (according to the method set out in BS EN 15403), CHNSO and inorganic contaminants. The oxygen content was
25 calculated by difference (100% - $\sum$ (CHNS+ash)). Inorganic contaminants were determined based on ICP-OES. The moisture content and TAN value was also estimated using a Karl Fischer V20S and an Autotitrator T5 respectively, both produced by Mettler Toledo. **Table 6** shows the results of those analysis.

The high heating value (HHV) for the bio-oil was also estimated using the Boie's equation (equation 3)

$$\text{HHV (MJ/Kg)} = 0.3419\text{C} + 1.11783\text{H} + 0.1005\text{O} - 0.1034\text{N} \quad (3)$$

Component	Unit	Value
C	wt. %	62.6
H	wt. %	8.28
N	wt. %	4.54
S	wt. %	0.66
O	wt. %	18.32
Ash	wt. %	5.6
Moisture	wt. %	3.68
TAN	mg KOH/g	5.88
HHV	MJ/Kg	31.64
Al	mg/Kg	760
Ca	mg/Kg	4700
Cr	mg/Kg	3.9
Cu	mg/Kg	53
Fe	mg/Kg	2200
K	mg/Kg	250
Mg	mg/Kg	660
Mn	mg/Kg	30
Na	mg/Kg	280
Ni	mg/Kg	5.0
P	mg/Kg	3000
Si	mg/Kg	190
Sn	mg/Kg	8.2
Ti	mg/Kg	14
Zn	mg/Kg	120
Zr	mg/Kg	3.3

Table 6. Characterization of a bio-oil obtained from a HTL reaction on sample E3, at 325 °C, 20 minutes of residence time and 18 MPa (180 bar) of pressure.

The reproducibility of bio-oil produced and recovered from post anaerobic sewage sludge according to the hydrothermal liquefaction reaction claimed, under optimised conditions, was investigated by analysing the bio-oil produced from digested cakes collected over the course of 54 consecutive weeks from June 2022-June 2023, and comparing the composition of the bio-oil. The results are shown in **Table 6a**. Since submitting the original sample in summer 2021, the data for which is presented in **Table 6**, the separating protocol has been refined, leading to significantly less ash in the bio-oil (**Table 6a**).

Component	Unit	Mean	SD
C	wt. %	75.13	1.51
H	wt. %	9.64	0.15
N	wt. %	4.60	0.16
S	wt. %	1.49	0.23
O	wt. %	8.99	1.38
Ash	wt. %	0.16	0.17
Moisture	wt. %	9.28	3.37
LHV	MJ/kg	30.93	0.36
HHV	MJ/kg	36.89	0.36
Al	mg/kg	9.91	4.91
Ca	mg/kg	34.55	21.19
Cr	mg/kg	0.77	0.34
Cu	mg/kg	3.87	1.38
Fe	mg/kg	239.19	57.26
K	mg/kg	14.88	23.42
Mg	mg/kg	4.45	2.71
Mn	mg/kg	0.70	0.32
Na	mg/kg	24.74	34.27
Ni	mg/kg	3.47	1.66
P	mg/kg	1.19	1.89
Si	mg/kg	95.93	31.19
Sn	mg/kg	10.32	1.67
Ti	mg/kg	5.76	1.22
Zn	mg/kg	6.53	2.04
Zr	mg/kg	0.25	0.09
As	mg/kg	3.12	2.37
Cd	mg/kg	0.06	0.05
Co	mg/kg	0.78	0.20
Pb	mg/kg	0.15	0.05
Hg	mg/kg	0.08	0.08
Mo	mg/kg	1.00	0.85
Se	mg/kg	0.39	0.13
Tl	mg/kg	0.06	0.05

Table 6a. Compositional analysis of 54 samples of bio-oil produced through the hydrothermal liquefaction process. The digested cakes, used as feedstock for these experiments, were collected weekly for 54 consecutive weeks from June 2022-June 2023. The High Heating Value (HHV) for the biocrude was estimated using the Boie’s equation and the Low Heating Value (LHV) was estimated using the equation $LHV\ (MJ/Kg) = HHV - 2.44(W + 8.9H)$.

Hydrotreated Bio-oil

The bio-oil was hydrotreated and then analysed to determine the various fractions of useful fuels contained therein. Analysis of a sample suggested that the particular sample of hydrotreated bio-oil contained 9% hydrocarbons suitable for bio-naphtha, 22.3% hydrocarbons suitable for Jet fuel (140°C to 235°C) and 68.7% hydrocarbons suitable for heavy fuel. Figure 8 shows the simulated distillation curve for the hydrotreated bio-oil and **Table 7** provides details on the various fuel fractions.

Boiling point range (°C)	Percentage of composition (wt%)
27.8 to 193	8.14
193 to 271	23.17
271 to 321	16.6
321 to 425	30.23
425 to 564	9.79
>564	3.67

Table 7 – Hydrocarbon fractions of the hydrotreated bio-oil based on boiling point, data obtained from the simulated distillation curve shown in Figure 8.

Sustainable Aviation Fuel (SAF) cut

The hydrocarbon types found in four samples A to D of HTL sewage-derived sustainable aviation fuel (SAF) are compared in **Table 8**.

Component	Sample A	Sample B	Sample C	Sample D
Paraffins	34.72	74.1	41.4	50.6
Monocycloparaffins	47.77	16.8	39.1	26.1
Dicycloparaffins	11.77	5.5	9.9	3.1
Tricycloparaffins	0.66	1.7	0.6	0.2
Total cycloparaffins	60.14	24.0	49.6	29.4
Alkylbenzenes	2.47	1.9	4.8	14.9

Indans and tetralins	1.93	0.0	3.5	4.6
Indenes	0.06	0.0	0.2	0.03
Naphthalene	0.10	0.0	0.0	0.0
Alkyl naphthalenes	0.05	0.0	0.0	0.0
Acenaphthenes	0.34	0.0	0.1	0.06
Acenaphthylenes	0.00	0.0	0.0	0.0
Tricyclic aromatics	0.20	0.0	0.4	0.5
Total Aromatics	5.14	1.9	9.0	20
Total (all)	100	100	100	100

Table 8 – Hydrocarbon types found in four samples A to D of HTL sewage-derived sustainable aviation fuel (SAF) sample in wt%.

Effect of operational variables on hydrocarbon composition

5 The effect of operational variables, such as residence time and bio-oil-to-catalyst ratios, on hydrocarbon composition was investigated. By tuning the catalytic upgrading conditions, it is possible to control the distribution of hydrocarbons (*i.e.* n-alkanes, iso-alkanes, monocycloalkanes, polycycloalkanes, aromatics) without significantly affecting the average carbon number, which was generally similar to the average carbon number
10 for fossil aviation fuel (11.5).

Different hydrocarbon types impart different fuel properties and thus influence the fuel quality and suitability for a given application. For example, specific energy may be enhanced by the compositional fraction from the n- and iso-alkanes, energy density may
15 be enhanced by the compositional fraction of cycloalkanes and aromatics, and the freeze point may be enhanced by the presence of iso- and cyclo-alkanes and aromatics. For legacy reasons, aircraft may require some level of aromatics for seal swelling to prevent fuel line leaks. Sooting is a major downside of having a high aromatics fraction, thus aromatic content should be maintained to the minimal amount required to avoid sooting.

20 A range of fuel properties from a representative SAF sample have been measured and are presented in **Table 8a**.

Fuel Property	Unit	Result
Flash point	°C	50
Density at 15 °C	kg/m ³	810
Density at 0 °C	kg/m ³	820
Density at -20 °C	kg/m ³	820

Density at -40 °C	kg/m ³	850
Freezing point	°C	-56.5
Viscosity -40 °C	mm ² /s	8.23
Viscosity -20 °C	mm ² /s	4.21
Viscosity 0 °C	mm ² /s	2.53
Paraffins	mass %	38
Cycloparaffins	mass %	59.7
Aromatics	mass %	2.3
Naphthenes	mass %	< 1.0
Tetralins and Indans	mass %	<18.55
Nitrogen	mg/L	1
Metals (Al, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Sn, Sr, Ti, V, Zn)	mg/kg	< 0.1 % for all metals analysed
Halogens	mg/kg	< 0.1 % for all halogens analysed
Surface Tension	Mn/m	26.91
Surface Tension Temperature	°C	20.7

Table 8a. Measured fuel properties and trace contaminants (metals and non-hydrocarbon composition) for a representative neat SAF sample

5 The SAFs produced according to the present invention are similar in many ways to fossil derived Jet A/A1 fuels. However, the SAFs produced according to the method of the invention may be high in aromatics relative to most other SAF pathways, but lower than those found in fossil derived aviation fuel. This is desirable since existing aviation engines are designed to consume fuels containing between 8 and 25wt% aromatic compounds, and thus it may be possible to utilise SAF produced according to the present invention in higher proportion in any blended aviation fuel. A further advantage is that higher aromatic contents are known to produce higher quantities of soot, and thus the present SAF would provide a beneficial reduction of soot production over existing fossil aviation fuels.

15 Bio-naphtha cut

Bio-naphtha is a sustainable alternative to petroleum-derived naphtha and can be used for many of the same applications. For this reason, the bio-naphtha cut from the process of the invention is of great value. One of the primary applications for naphtha is its use

as a precursor to gasoline and other liquid fuels. The motor octane number (MON) and research octane number (RON) of naphthas are used to assess their viability for such an application, as they provide insight on their performance as a fuel at high and low speeds and temperatures, respectively.

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The data for naphtha cuts, presented in **Table 9**, demonstrates that the hydrotreating conditions influences the MON but has a limited impact on the RON and the molar Carbon/Hydrogen ratio and the estimated Net and Gross heat.

	Units	Sample N1	Sample N2
MON	N/A	69.18	58.57
RON	N/A	77.02	77.36
C/H	Atomic ratio	0.53	0.53
Net Heat ^a	MJ/kg	43.22	43.31
Gross Heat ^a	MJ/kg	46.48	46.58

^aCalculated.

10 **Table 9.** Compositional information and fuels properties of two different bio-naphtha cuts.

Bio-Char

The corresponding bio-char obtained from the hydrothermal liquifaction reaction was also analysed for ash content, CHNSO and inorganic contaminants. The oxygen content was
15 calculated by difference (100% - $\sum(\text{CHNS}+\text{ash})$). Inorganic contaminants were determined based on ICP-OES. **Table 10** shows the results of those analysis and compares it to the standard quality requirements for bio-char. This data shows that the bio-char is suitable for further use. A number of the inorganic contaminants fall within the limits required for high quality bio-char.

		Quality requirements for biochar			Experimental
	Suggested method	Unit	Standard grade	High grade	
Organic content	ASTM D4373-02; BS EN 13039	% of dry mass	>10*		19.4
Total carbon	BS EN 15104	% of dry mass	-		12.7
Hydrogen	BS EN 15104	% of dry mass	-		1.33
Hydrogen/organic carbon -ratio (optional)		Molar ratio	≤0.7		1.25
Oxygen/Organic carbon – ratio (optional)		Molar ratio	-		0.218
Carbon/Nitrogen ratio (optional)	BS EN 15104	Molar ratio	-		14.66
Total Nitrogen (optional)	BS EN 15104	% of dry mass	-		1.01
Total P (optional)	Modified dry ashing followed by ICP (Enders and Lehmann 2012)26 BS EN 13650	mg/kg	-		76000
Total Potassium (optional)	Modified dry ashing followed by ICP (Enders and Lehmann 2012) BS EN 13650	mg/kg	-		300
Total ash content (optional)	BS EN 13039 ASTM D1762-84	% of dry mass	-		80.6
Heavy metals					
Arsenic (As)		mg/kg	≤100	≤10	1.3
Cadmium (Cd)		mg/kg	≤39	≤3	2.3
Chromium (Cr)		mg/kg	≤100	≤15	18
Cobalt (Co)		mg/kg	-	-	
Copper (Cu)		mg/kg	≤1500	≤40	650
Lead (Pb)		mg/kg	≤500	≤60	11.7
Mercury (Hg)		mg/kg	≤17	≤1	<0.1
Manganese (Mn)		mg/kg	-	≤3500	460
Molybdenium (Mo)		mg/kg	≤75	≤10	
Nickel (Ni)		mg/kg	≤600	≤10	12.8
Selenium (Se)		mg/kg	≤100	≤5	
Titanium (Ti)		mg/kg	-	-	<0.1
Zinc (Zn)		mg/kg	≤2800	≤150	1800

Table 10. Characterization of a bio-char obtained from a HTL reaction on sample E3, at 325 °C, 20 minutes of residence time and 18 MPa (180 bar) of pressure (experimental column), compared to typical bio-char requirements.

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The reproducibility of the corresponding bio-char produced and recovered from post anaerobic sewage sludge according to the hydrothermal liquefaction reaction claimed, under optimised conditions, was investigated by analysing the bio-char produced from digested cakes collected over the course of 54 consecutive weeks from June 2022-June 2023, and comparing the composition of the bio-char. The results are shown in **Table 10a**.

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Component	Unit	Mean	SD
C	wt. %	15.54	1.28
H	wt. %	1.70	0.15

N	wt. %	1.20	0.11
S	wt. %	1.66	0.48
O	wt. %	0.72	0.87
Ash	wt. %	79.54	1.44
Moisture	wt. %	1.44	0.38
Al	mg/kg	17239.08	7771.25
Ca	mg/kg	117666.67	47117.44
Cr	mg/kg	210.73	209.61
Cu	mg/kg	741.92	234.95
Fe	mg/kg	59315.28	18457.93
K	mg/kg	1479.96	549.41
Mg	mg/kg	17635.43	26007.06
Mn	mg/kg	656.02	259.76
Na	mg/kg	448.78	224.67
Ni	mg/kg	323.42	388.98
P	mg/kg	61848.15	25561.63
Si	mg/kg	899.85	387.20
Sn	mg/kg	156.26	28.40
Ti	mg/kg	60.14	72.49
Zn	mg/kg	1967.68	577.21
Zr	mg/kg	84.76	20.39
As	mg/kg	4.65	1.83
Cd	mg/kg	5.65	0.85
Co	mg/kg	13.90	7.17
Pb	mg/kg	249.51	41.21
Hg	mg/kg	1.40	0.24
Mo	mg/kg	17.40	38.18
Se	mg/kg	7.59	1.71
TI	mg/kg	1.07	0.19

Table 10a. Compositional analysis of 54 samples of bio-char produced through the hydrothermal liquefaction process. The digested cakes, used as feedstock for these experiments, were collected weekly for 54 consecutive weeks from June 2022-June 2023. The High Heating Value (HHV) was estimated using the Boie's equation and the Low Heating Value (LHV) was estimated using the equation $LHV \text{ (MJ/Kg)} = HHV - 2.44(W + 8.9H)$.

Although the present invention has been described in detail, it should be understood that various changes, substitutions, and alterations are contemplated without departing from the principle and scope of the invention. Accordingly, the scope of the present invention defined herein and particularly the following claims should be interpreted in consideration of the appropriate equivalents. The terms "a", "an" and "the" do not preclude the presence of multiple referents, unless the context clearly dictates otherwise. Optional or optionally means that the feature or activity may or may not be present. Either is contemplated. In embodiments, the optional feature or features may be present. Alternatively, the optional feature or features may not be present. Ranges may be expressed herein as "from" one particular value, and/or "to" another particular value, which is intended to be inclusive of the end-points of the range.

CLAIMS:

1. A method for producing a hydrocarbon fuel, the method comprising:
 - (i) subjecting a slurry of waste material, comprising one or more of sewage sludge, animal slurry, microalgal culture pastes, papermill and palm oil mill effluents and abattoir waste, to a hydrothermal liquefaction reaction to obtain a hydrothermal liquefaction product, wherein the hydrothermal liquefaction reaction is carried out with a residence time of 15 to 25 minutes, at a temperature of 280 to 373°C and a pressure of from 18 MPa to 22 MPa;
 - (ii) separating a bio-oil from the hydrothermal liquefaction product; and
 - (iii) processing the bio-oil to provide a hydrocarbon fuel.
2. The method of claim 1, wherein the hydrocarbon fuel is one or more of: sustainable aviation fuel, marine fuel, road fuel, heating fuel, or generator fuel.
3. The method of any one of the preceding claims, further comprising preparing a slurry of waste material prior to hydrothermal liquefaction, comprising adding a diluent to said waste material, and optionally, mixing or homogenising said slurry.
4. The method of any one of the preceding claims, wherein the waste material comprises sewage sludge, and wherein the sewage sludge comprises post-anaerobic digestion sewage sludge.
5. The method according to claim 4, wherein the sewage sludge, prior to being used to prepare a slurry, has a solids content of 20 wt% to 30 wt%.
6. The method according to any one of the preceding claims, wherein the slurry of waste material has a dry solids content of 20 wt% or less, preferably wherein the slurry of waste material has a dry solids content of from 10 - 20 wt%.
7. The method according to any preceding claim, wherein hydrothermal liquefaction reaction comprises subjecting the slurry of waste material to a temperature of from 300 to 350 °C.

8. The method according to any preceding claim, wherein the hydrothermal liquefaction reaction comprises subjecting the slurry of waste material to a pressure of from 19 to 21 MPa (190 to 210 bar), or 20 MPa (200 bar).
- 5 9. The method according to any preceding claim, wherein the slurry of waste material has a residence time of at least 16, 18, or 20 minutes in the hydrothermal liquefaction conditions.
- 10 10. The method according to any preceding claim, wherein the separation comprises using an organic solvent and wherein the organic solvent is separated via evaporation, reclaimed, and recycled.
- 15 11. The method according to any preceding claim, further comprising separating a bio-char from said hydrothermal liquefaction product and optionally, processing the bio-char to obtain a refined bio-char.
12. The method according to any preceding claim wherein processing the bio-oil to provide a hydrocarbon fuel comprises hydrotreating the bio-oil.
- 20 13. The method according to claim 12, wherein hydrotreating the bio-oil comprises hydrodeoxygenation of the bio-oil at a temperature of from 360 to 400 °C and a pressure of from 100 to 130 bar in the presence of a transition metal-based sulphided catalyst.
- 25 14. The method according to any preceding claim, wherein processing the bio-oil to provide a hydrocarbon fuel comprises fractionation of and/or hydrocracking the bio-oil.
- 30 15. The method according to claim 14, wherein the fractionation and/or hydrocracking produces an aviation fuel and a heavy fuel, and wherein the method further comprises recycling the heavy fuel to the fractionation and/or hydrocracking reactions to increase the yield of aviation fuel.
- 35 16. The method according to claim 15, wherein the fractionation and/or hydrocracking of the bio-oil also produces a bio-naphtha.

17. The method according any preceding claim, wherein the hydrothermal liquefaction reaction and/or the separation of the hydrothermal liquefaction reaction product produces off-gases, and wherein the method comprises using the off-gases or a component thereof as a feedstock for generating syngas, for e-fuel production, and/or for burning the off-gases or a component thereof in a heat recovery unit and supplying energy to the hydrothermal liquefaction reaction.
18. A hydrocarbon fuel produced according to any of claims 1 to 17, wherein the hydrocarbon fuel is sustainable aviation fuel.
19. The hydrocarbon fuel according to claim 18, wherein the content of monocycloalkanes is greater than 10wt% and/or wherein the content of polycycloalkanes is greater than 5wt% and/or wherein the content of aromatic compounds is greater than 10wt%.
20. An apparatus for producing sustainable aviation fuel, the apparatus comprising:
a hydrothermal liquefaction reactor configured to receive the slurry of waste material and conduct a hydrothermal liquefaction reaction on the slurry to produce a hydrothermal liquefaction product;
a separation unit configured to receive the hydrothermal liquefaction product and separate a bio-oil from the hydrothermal liquefaction product;
a processing unit configured to receive the bio-oil and process the bio-oil to produce a hydrocarbon fuel.
21. The apparatus according to claim 20 further comprising a mixer configured to prepare a slurry of waste material.
22. The apparatus according to claim 20 or 21, wherein the processing unit comprises a hydrotreating unit configured to hydrotreat the bio-oil.
23. The apparatus according to any one of claims 20 to 22, wherein the processing unit comprises a fractionation unit configured to separate the bio-oil to provide a sustainable aviation fuel and other fuel products; and/or wherein the processing unit comprises a hydrocracking unit configured to crack the bio-oil to provide a sustainable aviation fuel and other fuel products.

24. The apparatus according to claim 23, wherein the processing unit comprises a recycling line configured to recycle at least some of the other fuel products to the fractionation unit, hydrocracking unit, and/or hydrotreating unit.
- 5
25. The apparatus according to any one of claims 20 to 24, wherein the processing unit comprises a heat recovery unit configured to burn off gases produced from the hydrothermal liquefaction reaction and to supply energy to the hydrothermal liquefaction reactor and/or the processing unit.